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(54) PROCESS FOR THE MANUFACTURE OF INSOLUBLE SYNTHETIC PRODUCTS BASED ON POLYESTER-POLYURETHANE-EPOXIDE RESINS

(71) We, REICHHOLD-ALBERT-CHEMIE AKTIENGESELLSCHAFT, a Body Corporate organised and existing under the laws of Western Germany, of Iversstrasse 57, 2 Hamburg 70, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

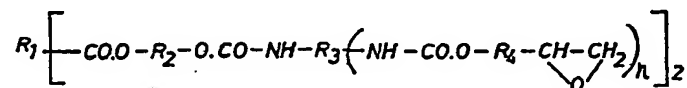
The invention relates to a process for the manufacture of synthetic resins based on novel epoxide compounds, which contain ester groups and urethane groups and which can be reacted in the conventional manner, by thermal polymerisation or by reaction with compounds which possess functional groups capable of reaction with epoxide groups, to give end products with good properties. The reaction can be carried out in the presence of unsaturated polymerisable monomers and/or reactive diluents.

It is known to manufacture epoxide compounds by reaction of a diisocyanate (for example toluylene-diisocyanate) with glycidol in a molar ratio of 1:2 (A. A. Berlin and A. K. Dabagova, Vysokomolekulyarny Soedinenya, 1, 946—50 (1959), German Patent 862,888).

Furthermore, polyurethane-diglycidyl-ethers are known which have been manufactured from 1 mole of polyalkylene-etherglycols, 2 moles of organic diisocyanates and 2 moles of a component which possesses a hydroxyl group and an epoxide group (U.S.A. 2,830,038).

Further, polyurethane-diglycidyl-ethers are known which are manufactured via the monochlorhydrin-ether of the diol, the dehydrohalogenation to give the monoglycidyl-etheralcohol and its reaction with diisocyanate, optionally with polyether-alcohols being simultaneously present (see Jellineck, Advances in the Field of Plasticisation of Aromatic and Cycloaliphatic Epoxide Resins, 2nd International Conference on Glass-fibre reinforced Plastics and Casting Resins in Berlin, 13, — 18.3.1967).

According to the present invention there is provided an epoxide compound of the formula



wherein R_1 represents the residue of maleic acid phthalic acid, or terephthalic acid after removal of carboxylic acid groups, R_2 represents the residue of bis-(hydroxymethyl)-tricyclodecane or hydroxy methylstearyl alcohol after removal of hydroxyl

[Price 25p]

groups, R_2 represents an aliphatic hydrocarbon radical or a cyclo aliphatic, aromatic, alkyl aromatic or heterocyclic hydrocarbon radical with 1 to 4 rings, R_1 represents an alkylene radical containing 1 to 6 carbon atoms, or a radical derived from a glycidyl ester of an hydroxy-acid or from a monoglycidyl ether of a polyhydric alcohol or phenol, and n is 1 to 3.

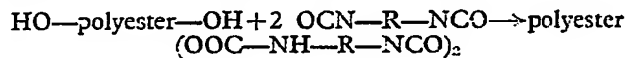
Where R_2 represents an aromatic or cyclic radical, the ring or rings may be optionally substituted with alkyl or alkoxy groups having 1 to 15 carbon atoms, methane groups, carbonyl groups or halogen atoms. R_2 may also represent radicals containing a number of condensed or non-condensed rings.

The invention includes a process for the preparation of the above epoxide compound, which comprises reacting an adduct of a di- or polyisocyanate and a polyester with a compound which contains at least one hydroxyl group and at least one epoxide group, said adduct having at least two isocyanate groups and said polyester being derived from the dicarboxylic acid of R_1 and one or more diols of R_2 .

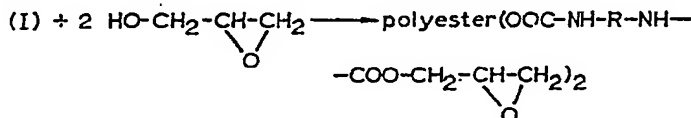
The polyesters employed for the manufacture of the adducts are appropriately obtained by reaction of 1 mole of the dicarboxylic acid and 2 moles of the diol.

To manufacture the epoxide compounds, 1 mole of the adduct with terminal NCO groups is in particular reacted, with 2 moles of a compound containing a hydroxyl group and an epoxide group.

To illustrate the method of manufacture of the new polyester-polyglycidyl-urethanes, the method of manufacture for the particular example of the "polyester-diglycidyl-urethane" from bifunctional derivatives (diisocyanate, diol, dicarboxylic acid and a compound which contains an epoxide group and a hydroxyl group, for example glycidol) is explained in the following reaction scheme:



(I)



polyester-diglycidyl-urethane.

According to the reaction scheme, 2 moles of a diisocyanate are reacted in a known manner with one mole of a polyester with terminal hydroxyl groups to give a polyester-diurethane adduct (I) having terminal NCO groups. The reaction of one mole of (I) with two moles of glycidol is preferably carried out in the presence of solvents (for example benzene). The reaction temperature should not be higher than 110°C (preferably 80°C).

The polyester used, having at least 2 hydroxyl groups, is manufactured according to generally known processes with an excess of the polyhydric alcohol component. The suitable molar ratio of the polyhydric alcohol to the polycarboxylic acid is 2:1 to 4:3, preferably 2:1 to 3:2.

The reactions, which are in themselves known, for the manufacture of the new epoxide compounds always take place quantitatively. It is of course also possible to employ mixtures of two or more of the dicarboxylic acids at a time.

As isocyanate components, aliphatic and cycloaliphatic as well as aromatic diisocyanates or polyisocyanates or combinations of these types are used. The cyclic compounds here comprise both condensed and non-condensed systems. In the latter, several rings can be linked to one another by hetero-atoms or polyfunctional groups. At the same time it is also possible to employ mixtures of two or more diisocyanates or polyisocyanates and also polyurethanes with excess NCO groups, for example phenyl-1,4-diisocyanate, toluylene-2,4-diisocyanate, toluylene-2,6-diisocyanate, 3,3'-bis-toluylene-4,4'-diisocyanate, 3,3'-dichlorodiphenyl-diisocyanate, 3,3' - dimethoxy - 4,4'-diphenyl - diisocyanate, 4,4' - dimethyl - 3,3' - diisocyanatodiphenylurea, 3,3' - dimethyl - 4,4' - diphenyldiisocyanate, 4,4' - diphenyl - diisocyanate, 4,4' - diphenylmethane - diisocyanate, hexamethylene-1,6-diisocyanate, 1 - methyl - 2,6 - phenyldiisocyanate, 1 - methyl - 2,4 - phenyldiisocyanate, naphthalene - 1,5 - diisocyanate, octadecyl-diisocyanate, phenylurethane-diisocyanate, 2,4,4' - diphenyl - ether - triisocyanate, triphenylmethane - 4,4',4'' - triisocyanate, trimethyl-hexamethylenediisocyanate, and 3-isocyanatomethyl - 3,5,5 - trimethyl - cyclohexyl - isocyanate.

As compound with at least one hydroxyl group and one epoxide group it is for example possible to employ glycidol, 2-methylglycidol, glycidyl esters of hydroxycarboxylic acids, such as for example lactic acid, glycollic acid, hydroxy-pivalic acid, 4 - (β - hydroxyethoxy) - benzoic acid, 3 - chloro - 4(β - hydroxy - ethoxy) benzoic acid and also monoglycidyl-ethers of the abovementioned polyhydric alcohols or phenols, or of the diols or bisphenols.

The new epoxide compounds can be converted by thermal polymerisation, appropriately at temperatures above 110°C, into spatially crosslinked insoluble products.

Since the monomeric units possess several reactive epoxide groups, which react with various functional groups, they can be reacted, by a reaction which is in itself known, with dicarboxylic acids or polycarboxylic acids or their anhydrides and with aliphatic, cycloaliphatic, aromatic and heterocyclic amines, which contain at least 2 primary or secondary amino groups, to give spatially crosslinked insoluble end products. These compounds, generally known as so-called curing agents in the epoxide resin field, can be employed in stoichiometric amounts. Herein, 60 to 360%, preferably 140 to 240%, of the stoichiometrically required amount are appropriately used. Dicarboxylic acids or polycarboxylic acids or their anhydrides, especially maleic anhydride, are preferably employed as compounds with functional groups capable of reaction with epoxide groups.

The reaction can also be carried out with catalytic amounts, appropriately 0.1 to 5% by weight, of tertiary amines or so-called Lewis acids, relative to the epoxide compound.

The thermal polymerisation of the epoxide compounds according to the invention, or the reaction with compounds which possess functional groups capable of reaction with epoxide groups, can be carried out in the presence of unsaturated polymerisable monomers and/or so-called reactive diluents.

It is also possible to work in the presence of polymerisation initiators for the unsaturated polymerisable monomer, such as for example potassium persulphate, dibenzoyl peroxide, cumene hydroperoxide, cyclohexanone peroxide, di-*t*-butyl peroxide and azodiisobutyronitrile.

Suitable unsaturated polymerisable monomeric compounds are especially aromatic and heterocyclic vinyl compounds such as styrene, methylstyrene, divinylbenzene, or vinylcarbazole; it is furthermore possible to use unsaturated hydrocarbons, ketones, ethers, carboxylic acids and their derivatives, for example 2-chlorobutadiene-(1,3), vinyl methyl ketone, vinyl phenyl ether, acrylic acid, acrylic acid esters, acrylonitrile, methacrylic acid, methacrylic acid esters, methacrylonitrile, α -chloracrylic acid, α -chloracrylic esters, vinylacetic acid, vinylacetone nitrile or vinyl acetate. Styrene is preferably employed.

Amongst the large number of reactive diluents known in the epoxide field, phenylglycidyl-ether, *i*-nonyl-glycidyl-ether, 2-ethylhexyl-glycidyl-ether and glycidol have proved particularly suitable.

The process according to the invention makes a large number of new types of epoxide resins with a very broad scale of mechanical and thermal properties available. The properties of the end products depend on the starting component employed. As a result of the large number of starting components, there are very many possible combinations.

For example, products with very good thermal properties are obtained if an epoxide resin pre-product of 2 moles of toluylenediisocyanate, 1 mole of polyester (manufactured from 1 mole of maleic anhydride and 2 moles of bis-(hydroxymethyl)-tricyclodecane) and 2 moles of glycidol are manufactured and cured with 30% by weight of maleic anhydride + 30% by weight of glycidol in 24 hours at 240°C. The product has a heat distortion point according to Martens of 240°C.

The product which is manufactured from 2 moles of hexanemethylenediisocyanate, 1 mole of polyester (manufactured from 2 moles of bis-(hydroxymethyl)-tricyclodecane and 1 mole of maleic anhydride) and 2 moles of glycidol, and which is cured with 30% by weight of maleic anhydride + 30% by weight of styrene in 24 hours at 180°C, has a heat distortion point according to Martens of 95°C.

Very good lacquer properties are for example shown by the product which is manufactured from 2 moles of toluylenediisocyanate, 1 mole of polyester (manufactured from 2 moles of bis(hydroxymethyl)-tricyclodecane and 1 mole of succinic anhydride) and 2 moles of glycidol, dissolved together with 25% by weight of isooctenyl-succinic anhydride in an acetone/chloroform mixture, applied on a sanded and degreased twice descaled metal sheet for deep drawing, and cured for 8 hours at 120°C. The films show very good adhesion and high hardness. On bending them over the smallest mandrel (2 mm) no damage to the films is detectable. The cross-

cut test gives a rating of Gt O B according to DIN 53151, draft of May 1964. The layer thickness is 18 μ and the pencil hardness is 8 H. The films are colourless and transparent.

Products with long-chain and branched diols in the polyester components, such as for example the mixture of the isomeric hydroxymethyl-stearyl alcohols (C_{17} -diol) can be used as reactive diluents with plasticiser properties.

The resin compositions according to the invention are suitable for use as casting, impregnating and laminating resins, especially in the electrical industry, as components of binders, above all of adhesives and synthetic resin mortars, as components of coating compositions, especially in the building industry, as lacquer raw materials for the manufacture of particularly chemically resistant lacquers, and as components of solvent-free lacquer systems, casting compositions, amongst others in mould construction and tool construction, and foams. They can contain known additives, such as for example fillers, colorants, or plasticisers, in the amount which are customary for these.

The examples which follow are intended to explain the invention in more detail:

Preproduct 1

Manufacture of a diester of phthalic anhydride and TCD-diol

148.1 g of phthalic anhydride (1 mole),
392.4 g of TCD-diol (2 moles),
5.3 g of p-toluenesulphonic acid and
530 g of xylene are mixed together.

The solution is boiled under reflux for a 1 l round flask possessing a stirrer and water separator, until the separation of water has ended. The solution is cooled and the solvent is stripped off on a rotary evaporator. The residue is transferred into a 500 ml round-neck flask and kept for 8 hours at 100°C in a waterpump vacuum, whilst stirring. After cooling, the product remains as a highly viscous, transparent residue. Acid number: 1 drop of 0.2 N NaOH causes phenolphthalein to change colour. Theoretical OH number: 207; effective OH number: 186.

Effective OH number/theoretical OH number: 0.89
Yield relative to phthalic anhydride, 96% of theory.

Preproduct 2

Manufacture of a diester-diol from maleic acid dimethyl ester and TCD-diol

110 g of maleic acid dimethyl ester (1 mole),
392.4 g of TCD-diol (2 moles) and
5 g of DBLZ (dibutyl-tin-dilaurate).

The mixture is heated to 180°C in a 500 ml two-neck flask with a water separator, under a constant stream of nitrogen. The temperature is maintained until the separation of methanol has ended (approx. 2 1/2 hours). Thereafter the melt is cooled to 120°C and treated for a further 6 hours in a waterpump vacuum. The product is a plastic, transparent substance.

Theoretical OH number: 237; effective OH number: 163.
Theoretical OH number/effective OH number: 0.69.

Yield, relative to maleic acid dimethyl ester, 97% of the theory.

Example 1

A. Preparation of the epoxide compound 1

50 g of phthalic acid-TCD-diol-diester (OH number=186) preproduct 1
29. g of toluenediisocyanate (0.16 mole) and
12.5 g of glycidol (0.16 mole).

29.2 g of toluenediisocyanate, dissolved in the same amount by weight of absolute benzene, are brought to the boil, whilst stirring, in a 500 ml three-neck round flask equipped with an internal thermometer, reflux condenser and dropping funnel. 50 g of phthalic acid-TCD-diol-diester, dissolved in 50 g of anhydrous benzene, are then slowly added dropwise to the heated solution, so that the internal temperature does not exceed 90°C (approx. 45 minutes). The mixture is then stirred for a further hour. Thereafter, 12.5 g of glycidol, again dissolved in the same amount by weight of benzene, are slowly added dropwise to the solution over the course of 20 minutes. The reaction mixture is stirred for a further hour and then cooled to room temperature. The solvent is stripped off as far as possible on a rotary evaporator. The

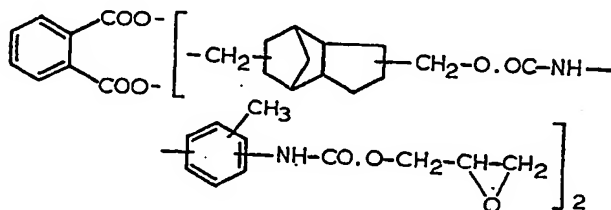
final drying is carried out in a drying cabinet at 90°C in a waterpump vacuum, until constant weight is reached.

The product is crystalline and colourless.

Its epoxide value is 1.61 m.equi/g.

Yield: 91.0 g of epoxide resin 1.

The epoxide resin 1 can be formulated as follows:



B. Production of the insoluble plastic

30% by weight of maleic anhydride, 20% by weight of styrene and 30% by weight of glycidol (% by weight relative to the epoxide resin 1 employed) are added to the epoxide resin 1. The mixture is heated to 70–80°C and poured into moulds. The samples are cured for 1 hour at 90°C+3 hours at 110°C+24 hours at 240°C. The cured samples have a Martens heat distortion point of 217°C.

Example 2

A. Preparation of the epoxide compound 2

55 g of maleic acid-TCD-diol-diester=preproduct 2 (OH number=163)

29.2 g of toluylenediisocyanate and

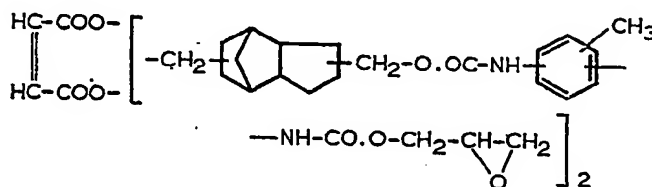
12.5 g of glycidol

are reacted, as described in example 1 A, to give the corresponding epoxide compound 2,

Epoxide value: 1.78 m.equi/g.

Yield: 110 g of epoxide resin 2.

The epoxide resin 2 can be formulated as follows:



B. Production of the insoluble plastic

100 g epoxide resin 2

27.5 g hexahydrophthalic anhydride

are melted together with caution at 70–80°C and stirred until homogeneous, 0.5 g 2,4,6-tris(dimethyl)-aminomethylphenol are added. The mixture is homogenised by stirring, and poured into a mould to give a plate of 10 mm thickness. Curing is achieved by heating the mould for 2 hours to 80°C, 100°C and 120°C. An insoluble plastic is obtained, having excellent strength and good electrical resistance.

Preproduct 3

97.09 g of terephthalic acid dimethyl ester (0.5 mole),

98.0 g of TCD-diol (0.5 mole),

73.3 g of a mixture of the isomeric hydroxymethyl-stearyl-alcohols (C₁₉-diol) and

2.6 g of dibutyl-tin-dilaurate

are reacted as described in preproduct 2 to give the corresponding hydroxy-ester compound.

OH number=102.

Yield relative to terephthalic acid dimethyl ester=98% of theory.

Example 3

A. Preparation of the epoxide compound 3

39.0 g of polyester=preproduct 3 (OH number=102),

29.2 g of toluylendiisocyanate and

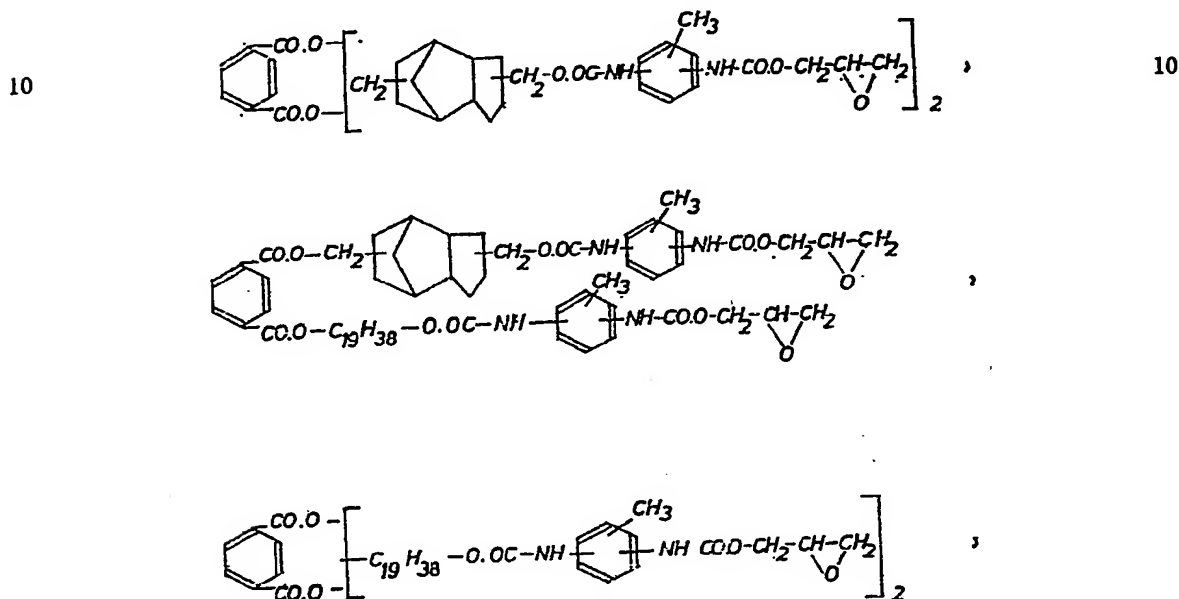
12.5 g of glycidol

are reacted as in example 1 A to give the corresponding epoxide compound 3.

Epoxide value: 0.9 m.equi/g.

Yield: 130 g of epoxide resin 3.

The epoxide resin 3 is a mixture of compounds that can be formulated as follows:



B. Production of the insoluble plastic

10 g of the epoxide compound 3 from example 3 A are dissolved in 50 ml of a mixture of equal parts of acetone and chloroform. Twice descaled metal sheet for deep-drawing, of 0.5 mm thickness, is sanded, degreased and repeatedly dipped into the solution. After 30 minutes' air-drying, the films are pre-cured for 1 hour at 70°C and cured for 8 hours at 120°C.

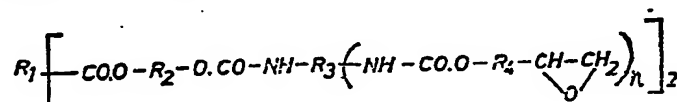
The finished films show the highest ratings in the mandrel bending test and in the cross-cut test. On bending over the smallest mandrel (2 mm), no damage to the lacquer layers is detectable.

The cross-cut test gives a rating of Gt O B according to DIN 531 51, draft of May 64. The film thickness is 20 μ and the pencil hardness 9 H. The films are colourless and transparent.

From the example and the resin formulations given above it is obvious that, apart from the new epoxide compounds, residues of unreacted or only partly reacted raw materials, by-products, and compounds of higher molecular weight may be present. These however do not interfere with the commercial use of the reaction products and with the conversion to the plastics.

WHAT WE CLAIM IS:—

1. An epoxide compound of the general formula



wherein R_1 represents the residue of maleic acid phthalic acid, or terephthalic acid after removal of carboxylic acid groups, R_2 represents the residue of bis-(hydroxy-

- 5 methyl)-tricyclodecane or hydroxy methyl-stearyl alcohol after removal of hydroxyl groups, R_3 represents an aliphatic hydrocarbon radical or a cyclo aliphatic, aromatic, alkyl aromatic or heterocyclic hydrocarbon radical with 1 to 4 rings, R_4 represents an alkylene radical containing 1 to 6 carbon atoms, or a radical derived from a glycidyl ester of an hydroxy-acid or from a monoglycidyl ether of a polyhydric alcohol or phenol, and n is 1 to 3. 5
2. A compound according to claim 1 wherein R_3 is a methyl-phenylene radical.
3. A compound according to claim 1 or 2 wherein R_4 is a methylene radical.
- 10 4. A compound according to claim 1 substantially as described herein. 10
5. A process for the preparation of an epoxide compound as claimed in any one of the preceding claims which comprises reacting an adduct of a di- or polyisocyanate and a polyester with a compound which contains at least one hydroxyl group and at least one epoxide group; said adduct having at least two isocyanate groups and said polyester being derived from the dicarboxylic acid of R_1 and one or more diols of R_2 .
- 15 6. A process according to claim 5 in which the diisocyanate is toluylene diisocyanate. 15
7. A process according to claim 5 or 6 in which the compound containing an epoxide group and an hydroxyl group is glycidol.
- 20 8. A process for the production of an insoluble plastics material which comprises cross-linking one or more epoxide compounds as claimed in any one of claims 1 to 4 by heating and/or by reacting said epoxide compound with a curing agent having a plurality of functional groups which are reactive with epoxide groups. 20
9. A process according to claim 8 which is carried out in the presence of an unsaturated polymerizable monomer and/or a reactive diluent.
- 25 10. A process according to claim 9 in which the polymerizable monomer is an aromatic or heterocyclic vinyl compound. 25
11. A process according to claim 9 or 10 in which the reactive diluent is glycidol or a glycidyl ether.
- 30 12. A process according to any one of claims 9 to 11 which is carried out in the presence of a polymerization initiator for the unsaturated polymerizable monomer. 30
13. A process according to any one of claims 8 to 12 in which the curing agent is a di- or polycarboxylic acid or anhydride.
14. A process according to claim 13 in which the dicarboxylic acid anhydride is maleic anhydride.
- 35 15. A process for the preparation of epoxide compounds substantially as described with reference to the Examples. 35
16. A process for the production of insoluble plastics materials substantially as described with reference to the Examples.

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